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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C08F 299/00, C09D 5/03 C08F 8/14, C09D 4/06 C09D 133/04	A1	(11) International Publication Number: WO 93/25596 (43) International Publication Date: 23 December 1993 (23.12.93)
(21) International Application Number: PCT/NL93/00120 (22) International Filing Date: 7 June 1993 (07.06.93) (30) Priority data: 9200542 10 June 1992 (10.06.92) BE (71) Applicant (for all designated States except US): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). (72) Inventor; and (75) Inventor/Applicant (for US only): WITTE, Franciscus, Maria [NL/NL]; Albrecht Thaelaen 70, NL-3571 EH Utrecht (NL). (74) Agent: PEELS, Robertus, Elisabeth, Jacobus; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).		(81) Designated States: AU, BB, BG, BR, CA, CZ, FI, HU, JP, KP, KR, KZ, LK, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: RESIN FOR POWDER COATINGS FOR USE AS A TOP COAT IN THE AUTOMOTIVE INDUSTRY AND TOP-COATED AUTOMOTIVE SUBSTRATES (57) Abstract The invention relates to a resin for powder coatings for use as a top coat in the automotive industry. The invention also concerns top-coated automotive substrates. The resin is an acrylate polymer with several side chains containing unsaturated groups and the amount of unsaturation in the unsaturated acrylate resin is between 213 and 1400 g per mol unsaturated group. The unsaturated group is a (meth)acrylate ester group, an allyl group, a vinyl group or an anhydride containing unsaturated group. The resin results in powder coatings having properties, which makes them very suitable in the automotive industry, especially for use as clear top coats.		

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- 1 -

RESIN FOR POWDER COATINGS FOR USE AS A TOP COAT IN THE
AUTOMOTIVE INDUSTRY AND TOP-COATED AUTOMOTIVE SUBSTRATES

The invention relates to a resin for powder coatings for use as a top coat in the automotive industry.

5 The invention also concerns top-coated automotive substrates.

The top coat or finish coat is the coating intended to be the last coat applied in a coating system and is usually applied over a primer, a basecoat or surfaces.

10 The clear top coats which, according to the present state of the art in the automotive industry, are used as a two-component system are solvent-containing paint systems based on acrylate resins cured with isocyanates. In order to meet the requirements regarding the reduction in solvent
15 emissions, so-called high-solids systems are already being used. The only way to reduce solvent emissions still further is to use powder coatings for clear automotive coatings (Lattke, E. "Pulverlack am Auto; Aus der Sicht der Autoindustrie", presented at "Der Pulvertreff '92, January
20 23, 1992, München"; JOT-Veranstaltungen, pages 1-11).

Powder paint systems for automotive top coats must meet the same stringent performance standards set for the solvent-containing systems. These requirements include for instance flow, chemical resistance, gloss and outdoor
25 durability (Kinza, W. "Pulverklarlack für die Karosseriebeschichtung", presented at "Die EPS-Praxis 1991, November 25 1991, Bad Neuheim"; Schriftenreihe Praxis-Forum, Fachbrochure Oberflächentechnik 27/91, pages 49-55).

It is an object of the present invention to provide
30 a resin which results in these properties at a curing temperature of less than 150°C. The presently available powder resin systems do not satisfy the required combination

- 2 -

of properties. Some properties can be obtained with systems based on an acid-epoxy curing reaction, but the required
5 combination of good flow, good chemical resistance, high gloss, high scratch resistance, good mechanical properties and good outdoor durability remains a desired but still elusive objective for powder coatings. With systems based on
10 polymers containing hydroxyl groups and curing agents containing blocked isocyanate groups, too, several of the above-mentioned properties can be obtained. However, the usual temperature (above 170°C) at which these systems must be cured is far too high for application as a (clear) topcoat for automotive applications.

15 It is for example elucidated in the article 'Powder Coatings in Europe' by Morandini (Pitture e Vernice 9/88, p. 70), that it is yet always an aim to find resins for the preparation of powder coatings that enable polymerisation or curing at lower temperatures, for example for 10-30 minutes
20 at 130°C.

Therefore it is the object of the present invention to provide a binder composition which can be cured at relatively low temperatures and which, moreover, gives a combination of said desired properties. The powder coating
25 have to result in a clear top coat on exterior parts in the automotive industry.

The invention is characterized in that the resin is an acrylate polymer having several side chains containing unsaturated groups and the amount of unsaturation in the
30 unsaturated acrylate resin is between 214 and 1400 g per mol unsaturated group.

More preferably this amount of unsaturation (WPU) is between 350 and 1000 gram per mol unsaturated group.

When applying the resin according to the invention
35 the curing can be effected both thermally and via radiation (UV and EB) at temperatures between for example 100°C and 150°C. The powder coatings obtained have good flow properties, good mechanical properties, good gloss, good impact resistance, good flexibility, good resistance to

- 3 -

chemicals and a very good resistance to petrol. The cured coatings are useful as a clear top coat in the automotive industry on exterior parts such as for example the body, hubcaps, wheels and doors.

Another advantage of the resin according to the invention is that no crosslinking agent need be used. This means that there are no problems arising from use of a toxic or mutagenic crosslinking agent.

The present invention offers the further important advantage of good outdoor durability of the coating as contrasted with UV-curing coatings which usually have a poor outdoor durability. As appears from for example page 19 of Journal of Radiation Curing (April 1984) this failure often came as a consequence of the individual components used in the formulated coatings.

The acrylate polymers having several side chains containing unsaturated groups which comprise the present powder coating resin can be obtained via a two-step process.

In a first step an acrylate polymer is prepared in a conventional polymerisation process in which also a certain portion of functional monomer is copolymerised to obtain a functionalized acrylate polymer. This functional monomer, which is usually present in amounts of between 3 and 60 wt.%, is preferably an epoxy-functional monomer, for example on the basis of glycidyl (meth)acrylate. However, acid-functional monomers, for example on the basis of (meth)acrylic acid, hydroxyl-functional monomers, for example on the basis of hydroxyethyl (meth)acrylate, isocyanate-functional monomers, for example on the basis of TMI (benzene,1-(1-isocyanato-1-methylethyl)-4-(1-methylethenyl) from American Cyanamid) or amine-functional monomers, for example on the basis of (meth)acrylamide, are also suitable monomers.

In the second step an addition reaction is carried out between the just described functionalized monomer of the acrylate polymer obtained from the first step and a compound containing a group that can react with said functional

monomer and that also contains an unsaturated group.

The compound can contain as group that can react
5 for example (meth)acrylate ester groups, allyl groups, vinyl groups and anhydrides containing unsaturated groups. Representative examples include (meth)acrylic acid, glycidyl (meth)acrylate, TMI, allyl glycidyl ether and maleic anhydride.

10 In the second step in this reaction the functionalized acrylate resin can be dissolved in a solvent, such as for example toluene, xylene or butyl acetate. The compound containing an unsaturated group that can react with the functionalized acrylate polymer is added at temperatures
15 of between for example 50°C and 150°C. Then the mixture is stirred for several hours. The progress of the reaction can be followed via titrations of for example acid groups or isocyanate groups.

Various addition reactions are possible in the
20 second step. Examples include reactions between an acid group and an epoxy-functional acrylate polymer, a hydroxyl group and an isocyanate-functional acrylate polymer, an isocyanate group and a hydroxyl-functional acrylate polymer, an anhydride group bound to an isocyanate and an amine-
25 functional acrylate polymer, an epoxy group and an acid-functional acrylate polymer or an epoxy group and an amine-functional acrylate polymer.

The reaction is preferably carried between an epoxy-functional acrylate polymer, such as
30 glycidyl(meth)acrylate polymer, and an acid group, such as (meth)acrylic acid.

The acrylate polymers can also be obtained via a multi-step process. In a multi-step process for example one of the isocyanate groups of a diisocyanate compound (such as
35 IPDI or H₁₂MDI) can react with a hydroxyl-functional (meth)acrylate monomer. The compound thus obtained, which contains an isocyanate group and a (meth)acrylate group, can then react with a hydroxyl-functional polymer such as an acrylate polymer that contains hydroxyethyl methacrylate as

the functional monomer.

The acrylate polymers according to the invention
5 can be cured for example thermally, via UV radiation or via
the electron beam (EB) method. These acrylate polymers are
preferably cured with UV radiation.

The technology and chemistry of curing by UV and
EB-curing is disclosed at pages 446-452 of JOCCA 1990 (11)
10 in the article "UV and EB curing" by S.J. Bett at al.

With the UV-radiation method a photoinitiator is
mixed with the acrylate polymer according to the invention.
This may be done both in a solvent or in the melt in the
extruder, the latter of which is preferred. Furthermore,
15 auxiliaries such as flow promoting agents may be added. Then
the paint can be applied to a plate or can be
electrostatically sprayed. In the latter case the plate is
placed in an oven and the powder is melted (this may also be
effected by means of heating via infrared radiation), after
20 which the panel, which is still hot, is cured under a source
of UV light or by EB-curing.

Suitable photoinitiators include for example
Irgacure™ (Ciba Geigy), Darocure™ (Merck) and Lucirine
TPO™ (BASF). Preferably, the initiators are solids and are
25 present in amounts of between 0.2 and 6 wt.-%.

A major advantage of this curing procedure is that
the softening of the powder paint (through heat) takes place
completely separately from the curing reaction (curing
through radiation). This means that powder coatings that
30 have extremely good flow properties can be made from the
present powder coating composition.

With the thermal curing method peroxides such as
for example alkyl peroxides, acyl peroxides, peroxyesters or
peroxyketals are mixed with the acrylate polymer according
35 to the invention. This can be done in solution or in the
melt in the extruder. Furthermore, auxiliaries such as
cobalt (for the acceleration of the peroxide decomposition),
flow promoting agents, degassing agents and pigments may be
added. After this the resin solution is applied to a plate

- 6 -

or the powder is electrostatically sprayed onto a plate and cured in an oven for a certain length of time.

5 The cured powder coating is hence obtained by causing unsaturated groups in the side chain of the acrylate polymers to react with one another, via for example thermal curing (addition of peroxides), curing with the aid of ultraviolet light (addition of a photoinitiator) or
10 electron-beam curing. That is why no special hardeners are necessary and no volatile components are released during the curing.

 The complete disclosure concerning acrylic powder coatings, parameters influencing powder coating properties
15 and the technology of production of powder coatings from Misev, Powder Coatings, Chemistry and Technology, on pages 162-167, 174-175 and 224-225 (John Wiley and Sons; 1991) is incorporated herein by reference.

 The usual additives, such as fillers, flow aids
20 and/or stabilizers and also pigments if desired, can be added to the coating systems, preferably during extrusion.

 Novel top-coated automobile parts comprise a substrate, e.g. a body panel or other top-coatable automobile parts (such as for example wheels, wheelcovers
25 and doors), having, if desired, a pigment layer or layers thereon and a clear top coat over the pigment layer or layers (if present) wherein the top coat comprises a solvent-free powder coating obtained from the binder composition according to the invention.

30 The powder coatings obtainable with the resin according to the invention can be applied on body parts, such as for example wheels, wheelcovers, fenders, doors, hoods and the like but can also be used on wood or plastic. The powder coatings of the present invention are also useful
35 as industrial top coats for general purposes, for top coats for machinery and equipment, especially top coats for metal, for example cans, household articles and other small pieces of equipment.

 US-A-3974303 relates to a method for forming

- 7 -

coating films which comprises coating a powder composition of a resin having unsaturated bonds. This resin may be, amongst many others, a vinyl or acrylic polymer having polymerisable unsaturated bonds. However, US-A-3974303 contains no suggestion that precisely the specific resins according to the present invention offer a solution to the aforementioned problems with respect to powder coatings in the automotive industry.

The invention is further described with reference to the following non-limiting examples.

Examples

15

Example I

Preparation of an acid-functional acrylate resin

A 2-litre reactor vessel, fitted with a thermometer, a stirrer and a reflux condenser, was filled with 500 g of butyl acetate. With stirring, the temperature was raised to reflux temperature while a stream of nitrogen was passed through the reactor. Then a monomer mixture consisting of 510 grams of methyl methacrylate, 300 grams of butyl acrylate and 190 grams of methacrylic acid was prepared. 55.5 grams of 2,2-azo-bis-isobutyronitrile (AIBN) initiator was dissolved in the mixture of the monomers of in total 1000 grams. This mixture was then supplied to the reactor in 3 hours. The temperature in the reactor was kept at reflux temperature. Two hours after the addition of the monomer mixture a separation vessel was included in the setup and the solvent was removed by gradually increasing the temperature and creating a vacuum. The product had an acid number (ISO 3682) of 107 mg of KOH/g of resin, the viscosity (η) measured with the aid of an Emila rheometer (dPa.s, 165°C) was 275 dPa.s, and the glass transition temperature (T_g , Mettler TA-3000, 5°C/min) was 51°C. The test procedures are described in the already cited book "Powder Coatings" at pages 284-300.

Example IIPreparation of a hydroxyl-functional acrylate resin

5 500 g of toluene was added to a 2-litre reactor vessel fitted with a thermometer, a reflux condenser and a stirrer. The monomer mixture consisted of 368 g of methyl methacrylate, 232 g of hydroxyethyl methacrylate, 200 g of butyl acrylate and 200 g of cyclohexyl methacrylate in which
10 30.27 g of AIBN was dissolved. According to the same method as in Example I a product was obtained that had a viscosity of 425 dPa.s (Emila, 165°C) and a T_g of 48°C.

Examples III-IV15 Preparation of an epoxy-functional acrylate resin

 500 g of toluene was added to the reactor as described in Examples I and II. The synthesis was carried out as described in Examples I and II. The monomer mixtures and the amounts of tert.-amyl peroxy-2-ethylhexanoate
20 initiator (Luperox 575™, Atochem) dissolved in them are indicated in Table I (in grams).

 In addition to the amounts of monomer and initiator, Table I also indicates the theoretical epoxy equivalent weight (EEW), the viscosity measured with the aid
25 of an Emila rheometer (dPa.s, 165°C) and the glass transition temperature (T_g , Mettler TA-3000, 5°C/min). The indicated Mn and Mw values were determined with the aid of GPC (gel permeation chromatography), using polystyrene as a standard.

- 9 -

Table I

5	III	IV	V	VI
MMA ¹⁾	500	500	400	500
BA ²⁾	100	100	100	150
CHMA ³⁾	200	200	100	250
10 GMA ⁴⁾	300	300	500	200
Luperox575 TM	47.5	76.0	64.7	64.7
EEW	520	520	312	781
Visc.	620	265	200	270
T _g (°C)	52	51	47	48
15 Mn	4300	3820	n.m. ⁵⁾	n.m.
Mw	10400	7590	n.m.	n.m.
D ⁶⁾	2.4	2.0		

20 where

1) MMA = methyl methacrylate

2) BA = butyl acrylate

3) CHMA = cyclohexyl methacrylate

4) GMA = glycidyl methacrylate

25 5) n.m. = not measured

6) D = Mw/Mn; polydispersity.

Example VII30 Preparation of an isocyanate-functional resin

250 g of toluene was added to the reactor as described in Examples I, II and III. The monomer mixture consisted of 180 g of methyl methacrylate, 155 g of TMI (American Cyanamid), 65 g of cyclohexyl methacrylate and 100 g of butyl acrylate in which 14.5 g of tert.-butyl perbenzoate was dissolved. The monomer mixture was added to the reactor in 4.5 hours. The reaction mixture was kept at reflux temperature and 3 hours after the addition of the monomer mixture 3 g of tert.-butyl perbenzoate was added to

- 10 -

the reactor. After 4 hours at reflux temperature a separation vessel was incorporated in the reactor and the
5 solvent was removed by increasing the temperature and creating a vacuum. The product had a viscosity (Emila, 165°C) of 100 dPa.s and a T_g of 52°C.

Example VIII

10 Preparation of an acrylate resin containing a glycidyl methacrylate ester group as the unsaturated side chain, through the addition of glycidyl methacrylate to an acid-functional acrylate resin

400 g of resin of Example I was dissolved in 400 g
15 of butyl acetate in the reactor as described in Examples I-VII. 0.4 wt.% tetramethylammonium chloride was added for the acid-epoxy reaction and 0.1 wt.% mono-tert.-butylhydroquinone (MTBHQ) to prevent polymerisation of the methacryl functionality. The reaction mixture was heated to
20 110°C with stirring. In one hour 109 g of glycidyl methacrylate (GMA) was added dropwise. At the moment that the acid number of the reaction mixture was lower than 10 mg of KOH/g of resin a separation vessel was incorporated in the reactor and the solvent was removed by increasing the
25 temperature and creating a vacuum. The final product had an acid number of 5 mg of KOH/g of resin and a T_g of 22°C.

Example IX

30 Preparation of an acrylate resin containing an allyl group as the unsaturated side chain, through the addition of allyl glycidyl ether to an acid-functional acrylate resin

400 g of resin of Example I was dissolved in 400 g
of butyl acetate in the reactor as described in the above
35 examples. 0.4 wt.% tetramethylammonium chloride was added to accelerate the acid-epoxy reaction and 0.1 wt.% mono-tert.-butylhydroquinone (MTBHQ) as an inhibitor to prevent polymerisation of the allyl functionality. The reaction mixture was heated to 110°C with stirring. In one hour 87 g

- 11 -

of allyl glycidyl ether was dropwise added to the reactor. When the acid number of the reaction mixture was lower than 10 g of KOH/g of resin, the solvent was removed as described in Example VIII. The product had an acid number of 8 g KOH/g of resin and a T_g of 13.5°C.

Example X

10 Preparation of an acrylate resin containing a vinyl group as the unsaturated side chain, through the addition of TMI to a hydroxyl-functional resin

521 g of resin of Example II was dissolved in 521 g of toluene in the reactor as described in the above examples. To this were then added 187 g of TMI, 0.4 wt.% dibutyltin laurate to accelerate the hydroxy-isocyanate reaction and 0.1 wt.% MTBHQ to prevent polymerisation of the vinyl functionality. The reaction mixture was heated to 80°C with stirring. When the NCO content (as determined via 20 dibutylamine titration) was lower than 0.2 wt.% the solvent was removed as described in Example VIII. The final product had an NCO content of 0.16 wt.% and a T_g of 28.5°C.

Example XI

25 Preparation of an acrylate resin containing a double bond derived from MA as unsaturated side chain, through the addition of maleic anhydride (MA) to a hydroxyl-functional resin

300 g of resin of Example II was dissolved in 300 g of toluene in the reactor described in the above examples. The reaction mixture was heated to 115°C. 52.5 g of MA was dissolved in 52.5 g of toluene and this solution was added to the reactor in an hour. When free MA was no longer detected (via determination of the acid number) the solvent 35 was removed as described in previous examples. The final product had an acid number of 78 g of KOH/g of resin and a T_g of 26°C.

Example XII

5 Preparation of an acrylate resin containing a
methacrylate ester group as unsaturated side chain, through
the addition of methacrylic acid to an epoxy-functional
resin

 In a reactor identical to that described in the
above examples 400 g of resin of Example III was dissolved
10 in 400 g of butyl acetate. To this were added 0.4 g of
tetramethylammonium chloride to accelerate the acid-epoxy
reaction and 0.1 wt.% MTBHQ to prevent the reaction of the
methacrylate functionality. The reactor contents were heated
to 115°C with stirring and 66 g of methacrylic acid was
15 added dropwise to the reactor in an hour. The reactor was
kept at 115°C until the acid number of the reaction mixture
was less than 10 mg of KOH/g of resin. The solvent was
removed as described above. The product had an acid number
of 3 g of KOH/g of resin and a T_g of 29°C.

20

Examples XIII-XV

Preparation of an acrylate resin containing an
acrylate ester group as unsaturated side chain, through the
addition of acrylic acid to the epoxy-functional resin

25 In the reactor described in the above examples the
indicated amount of resin (see Table II) of Examples IV, V
and VI was dissolved in butyl acetate so that a 50 wt.%
resin solution was obtained. The reaction was carried out in
a manner identical to that described in Example XII using
30 identical amounts of tetramethylammonium chloride and MTBHQ
by adding the amount of acrylic acid indicated in Table II
(in grams) to the reactor in an hour.

Table II

5	XIII	XIV	XV
resin of Example:			
IV	1000		
V		750	
10 VI			750
AA ¹⁾	137.7	173.1	69.2
AN ²⁾	2	3	2
WPU ³⁾	593	385	853
T _g (°C)	37	33	37
15 Mn ⁴⁾	4230	n.m. ⁶⁾	n.m.
Mw ⁴⁾	8770	n.m.	n.m.
D ⁵⁾	2.1		

20 where

1) AA = acrylic acid;

2) AN = acid number in g of KOH/g of resin;

3) WPU = theoretical equivalent weight in g of resin per unsaturated group;

25 4) Mn and Mw were determined via GPC (gel permeation chromatography) using polystyrene as a standard;

5) D = Mw/Mn; polydispersity;

6) n.m. = not measured.

30

Example XVI

Preparation of an acrylate resin containing a methacrylate ester group as unsaturated side chain, through the addition of hydroxyethyl methacrylate to an isocyanate-
 35 functional resin

In the reactor described in the above examples 345 g of resin of Example VII was dissolved in 345 g of toluene. To this were then added dibutyltin laurate to accelerate the hydroxy-isocyanate reaction and MTBHQ to prevent the

- 14 -

reaction of the methacrylate functionality. The reaction mixture was heated to 55°C with stirring and 68 g of hydroxyethyl methacrylate was added to the reactor in half an hour. When the NCO content (determined via dibutylamine titration) was lower than 0.2 wt.% the solvent was removed.

Example XVII

10 Thermal curing

Of the resins containing an unsaturated side group that are mentioned in Table III 50 wt.% solutions were made in butyl acetate or toluene, to which 1 wt.%, relative to 100% resin, peroxide (Trigonox 29B50™; AKZO) and 0.05 wt.%, relative to 100% resin, and cobalt (6% Co SiccatoI solution) were added. The resin solutions were applied to steel plates which were cured in an oven at 190°C for 20 minutes. The coatings eventually obtained were 30-50 µm thick. The curing was tested by measuring the acetone resistance of the coating by rubbing a wad of cotton wool saturated with acetone to and fro (100 times) over the surface of the coating. If the coating showed no visible effects or did not become soft, the coating was well cured and was qualified > 100 DR (double rubs). In the event of poorer resistance to acetone it is indicated after how many double rubs the coating was removed from the plate.

Table III

30 resin according
to example

VIII

XVI

35 acetone DR

> 100

> 100

Acrylate polymers containing a (meth)acrylate ester group as the unsaturated side chain hence yield powder coatings with an excellent acetone resistance after thermal curing.

Example XVIIICuring with the aid of UV radiation

5 The resins mentioned in Table IV were mixed in an extruder at 110°C with 2 wt.% photoinitiator Irgacure 184™ (Ciba Geigy) and 1 wt.% flow promoting agent (BYK 361™). The extrudate was ground and sieved, after which the fraction with a particle size of less than 90 micrometres was applied to a substrate with the aid of an electrostatic spraying apparatus. The powder-coated panels were placed in an oven at 150°C for 15 minutes, after which the panels, which had a temperature of between 100 and 125°C, were exposed to UV radiation. All panels were radiated using 2.0 J/cm². The flow properties of the coatings were visually assessed and the quality of the curing was determined by measuring the resistance to acetone as described above.

10 The resistance to petrol of the cured powder coatings was determined by placing a wad of cotton wool saturated with petrol on the coating, under a piece of glass, for 2 hours, after which the coating was visually inspected for any effects or discolouration. The durability of the cured powder coatings according to example XIII was measured using QUV artificial weathering apparatus (ASTM-G-53, lamp: UVB-313).

Table IV

resin	XIII	XIV	XV
flow properties	reasonable	very good	very good
acetone DR	> 100	> 100	> 100
resistance to			
petrol	very good	very good	very good
QUV (hr)	> 1500 ¹⁾		

1) after 1500 hours no loss of gloss or discolouration.

- 16 -

This shows that after UV curing acrylate polymers containing an acrylate ester group as the unsaturated side chain result in powder coatings with excellent flow properties and acetone resistance.

In automotive applications the excellent resistance to petrol and the large number of hours in the QUV artificial weathering apparatus without loss of gloss or discolouration are very favourable.

Example XIX

Curing with the aid of EB radiation

The resin of Example XIII was mixed with 1 wt.% flow promoting agent (BYK 163™) in an extruder at 110°C. The extrudate was processed as described in Example XVIII. The powder-coated panels were placed in an oven at 150°C for 15 minutes to fluidize the applied powder, after which the panels, which had a temperature of 100-125°C, were exposed to electron-beam radiation in an ESI electron curtain apparatus using a beam voltage of 180 kilovolt, a beam intensity of 4 mA and a cure dose of 15 mrad. A well-cured coating with very good flow properties was obtained and the coating was not affected after 100 acetone double rubs.

From this it can be concluded that an acrylate resin containing an acrylate ester group as the unsaturated group in the side chain can be cured thermally, via UV radiation and via EB radiation to yield a well-cured powder coating.

C L A I M S

- 5
1. Resin for powder coatings for use as a top coat in the automotive industry, characterised in that the resin is an acrylate polymer having several side chains containing unsaturated groups and the amount of
10 unsaturation in the unsaturated acrylate resin is between 214 and 1400 g per mol unsaturated group.
 2. Resin according to claim 1, characterised in that the amount of unsaturation is between 350 and 1000 g per mol unsaturated group.
 - 15 3. Resin according to any one of claims 1-2, characterised in that the unsaturated group is a (meth)acrylate ester group, an allyl group, a vinyl group or an anhydride containing unsaturated groups.
 4. Resin according to any one of claims 1-3, characterised
20 in that the resin is the product of the reaction between an epoxy-functional acrylate polymer and an acid group.
 5. Resin according to claim 4, characterised in that the epoxy-functional acrylate polymer is glycidyl (meth)acrylate polymer and the acid group is
25 (meth)acrylic acid.
 6. Use of a resin according to any one of claims 1-5 for the preparation of a powder coating for use as a clear topcoat on exterior parts in the automotive industry.
 7. Powder paint comprising a resin according to any one of
30 claims 1-5 and usual additives for use as a top coat in the automotive industry.
 8. Method for the preparation of a powder paint, characterised in that the softening of the powder coating based on a resin according to any one claims 1-5
35 takes place through heat and the curing takes place by UV or EB radiation.

9. A partially or wholly top coated automobile body part wherein said top coat is a powder coating obtained from
5 an acrylate polymer having several side chains containing unsaturated groups and the amount of unsaturation in the unsaturated acrylate resin is between 214 and 1400 g per mol unsaturated group.
10. A top-coated automobile part according to claim 9,
10 characterised in that the amount of unsaturation is between 350 and 1000 g per mol unsaturated group.
11. A top-coated automobile part according to any one of claims 9-10, characterised in that the unsaturated group
15 is a (meth)acrylate ester group, an allyl group, a vinyl group or an anhydride containing unsaturated group.
12. A top-coated automobile part according to any one of claims 9-11, characterised in that the resin is the product of the reaction between an epoxy-functional acrylate polymer and an acid group.
- 20 13. A top coated automobile part according to claim 12, characterised in that the epoxy-functional acrylate polymer is glycidyl (meth)acrylate polymer and the acid group is (meth)acrylic acid.
14. A partially or entirely coated wood, plastic or metal
25 substrate, wherein the coating is obtained from a powder coating which is based on a resin composition according to any one of claims 1-5.
15. A method of coating automobile parts which comprises applying to the substrate a top coat based on a resin
30 according to any one of claims 1-5.
16. Resin, use, method, powder paint and coated substrate as substantially described and/or further explained in the examples.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 93/00120

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C08F299/00; C09D5/03; C08F8/14; C09D4/06 C09D133/04		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C08F ; C09D ; C08J	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	US,A,3 974 303 (SEIGO IWASE ET AL.) 10 August 1976 cited in the application see claims see example 4 see column 3, line 45 - line 50 ----- -/--	1-8, 14, 16
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search 01 OCTOBER 1993		Date of Mailing of this International Search Report 19.10.93
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer PERSSON E.K.

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	CHEMICAL ABSTRACTS, vol. 86, no. 20, 16 May 1977, Columbus, Ohio, US; abstract no. 141733d, OZAWA HIROSHI ET AL. 'RESIN POWDER COATING COMPOSITIONS' page 93 ;column 1 ; see abstract & DATABASE WPI Derwent Publications Ltd., London, GB; AN 77-10120Y & JP,A,51 149 325 (MITSUI TOATSU CHEM INC) 23 December 1976 see abstract ---	1-5,7
A	EP,A,0 480 120 (MITSUI TOATSU CHEM INC) 15 April 1992 see claims see page 8, line 14 - line 22 ---	1-5,7
A	DE,A,2 163 660 (FORD-WERKE AG) 5 July 1973 see claims see examples see page 18, line 1 - line 12 ---	1-5
A	EP,A,0 029 596 (E.I.DU PONT DE NEMOURS AND COMPANY) 3 June 1981 see page 1, line 30 - page 2, line 17 see claims 1-4 -----	1,6,9,15

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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

NL 9300120
SA 76262

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The members are as contained in the European Patent Office EDP file on
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		JP-B- 54019895	18-07-79
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		JP-A- 56084767	10-07-81

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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